Syntheses and Structures of Mixed-Metal Sulfido Clusters Containing Trimetallic $M_2M'S_4$ (M = Mo, W; M′ = Pd, Pt) and Tetrametallic Cubane-Type $Mo_2Pd_2S_4$ Cores

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The reaction of the sulfido-bridged dimolybdenum or ditungsten complex $[M_2S_2(\mu_2\text{-}S)_2(S_2CNEt_2)_2]$ (M = Mo (**1a**), W) with an equimolar amount of $[M'(PPh_3)_4]$ (M′ = Pd, Pt) gave a series of mixed-metal sulfido clusters with a trimetallic M_2M' core $[M'(PPh_3)(\mu_2\text{-}S)_2\{M(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$. The X-ray diffraction study for $[Pt(PPh_3)(\mu_2\text{-}S)_2\{W(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ (**3b**) has disclosed the presence of a novel triangular framework, for which the two Pt−W edges are each bridged by one μ_2-S ligand and the remaining W−W edge is supported by two μ_2-S ligands. Cluster **3b** crystallized in the monoclinic system, space group $C2/c$ with $a = 13.718(3)$ Å, $b = 12.795(2)$ Å, $c = 43.798(2)$ Å, $\beta = 95.24(1)°$, and $Z = 8$. Refinement by full-matrix least-squares techniques gave final residuals $R = 0.052$ and $R_w = 0.038$. Treatment of $[Pd(PPh_3)(\mu_2\text{-}S)_2\{Mo(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ with an additional amount of $[Pd(PPh_3)_4]$ resulted in the formation of the cubane-type mixed-metal sulfido cluster $[\{Pd(PPh_3)\}_2\{Mo(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$, which was also obtained straightforwardly from the reaction of **1a** with 2 equiv of $[Pd(PPh_3)_4]$.

Introduction

The chemistry of transition metal−sulfur clusters[1] is now progressing rapidly owing to intimate relevance to certain biological[2] and industrial catalyses.[3] In this context, emphasis has been placed on the clusters containing the first-row transition metals and/or group 6 metals such as Mo and W. By contrast, syntheses and reactivities of noble metal−sulfur clusters are still poorly exploited, although a variety of stoichiometric and catalytic reactions are known to be promoted by noble-metal compounds.

We have continuously been interested in the unique reactivities displayed by the noble metal center(s) embedded in the metal−sulfur aggregates, and our recent studies have already demonstrated that the mixed-metal sulfido cluster containing a cubane-type $PdMo_3(\mu_3\text{-}S)_4$ core is capable of catalyzing the stereo- and regioselective addition of alcohols[4] or carboxylic acids[5a] to the alkynes with electron-withdrawing substituents as well as the intramolecular cyclization of alkynoic acids with remarkably high efficiency.[5b]

Stimulated by these findings, further studies have been undertaken to synthesize a series of mixed-metal sulfido clusters containing Pd or a congenerous noble metal Pt. Quite recently we have found two versatile synthetic routes leading to such clusters. One involves the reactions of the hydrosulfido-bridged dinuclear complexes $[Cp^*MCl(\mu_2\text{-}SH)_2MCp^*Cl]$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Ru, Rh, Ir) with various metal complexes affording an enormous body of $M_2M'(\mu_3\text{-}S)_2$ clusters,[6] while the other is the incorporation of one or two noble metals into the dinuclear complexes $[M_2S_2(\mu_2\text{-}S)_2(S_2CNEt_2)_2]$ (M = Mo (**1a**), W (**1b**)) affording the mixed-metal clusters with the $M_2M'(\mu_2\text{-}S)_4$ (M′ = Pd, Pt) or $Mo_2Pd_2(\mu_3\text{-}S)_4$ core. In this paper, we report in detail the reactions of the latter type. It is to be noted that most of the precedented metal−sulfido cluster cores have been constructed by the use of self-assembly systems, and the rational and reliable methods to form the desired metal−sulfur frameworks in satisfactory yields are still rare and desired to be exploited. Extension of the reaction system reported here to group 9 noble metals is now under investigation, the results of which will be described in a subsequent paper.

Results and Discussion

Formation of Trinuclear Clusters. Treatment of the dimolybdenum or ditungsten complex **1** with an equimolar amount of $[M'(PPh_3)_4]$ (M′ = Pd, Pt) in THF at room

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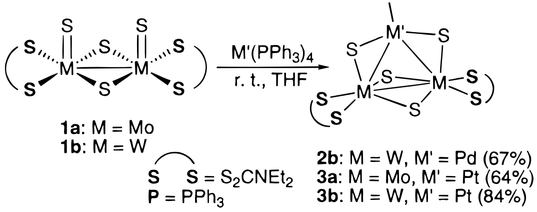
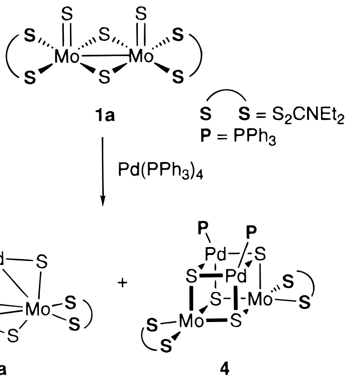
temperature afforded a series of triangular clusters [M′(PPh$_3$)(μ_2-S)$_2${M(S$_2$CNEt$_2$)}$_2$(μ_2-S)$_2$] (M = Mo, M′ = Pd (**2a**), Pt (**3a**); M = W, M′ = Pd (**2b**), Pt (**3b**)). Clusters **2b**, **3a**, and **3b** were readily isolated in an analytically pure form by recrystallization from benzene−hexane in moderate yields (eq 1).



(1)

However, **2a** obtained from the reaction of **1a** with [Pd(PPh$_3$)$_4$] has proved to be contaminated by a small amount of the tetranuclear cluster [{Pd(PPh$_3$)}$_2${Mo(S$_2$CNEt$_2$)}$_2$(μ_3-S)$_4$] (**4**; vide infra) concurrently produced (eq 2).



(2)

Although the reaction of **1a** with a less amount of [Pd(PPh$_3$)$_4$] (0.8 equiv) was attempted to suppress the formation of **4**, the **2a**:**4** ratio in the product mixture did not increase appreciably (ca. 10:1) and isolation of **2a** in a pure form was unsuccessful from this reaction mixture.

In the IR spectra of **2** and **3**, the characteristic ν (M=S) bands observed for **1a** (546 cm^{-1}) and **1b** (531 cm^{-1}) disappeared, indicating that the terminal M=S groups are no longer present in **2** and **3**. Involvement of the S$_2$CNEt$_2$ and PPh$_3$ ligands in the 2:1 ratio has been demonstrated by the ^{1}H NMR spectra, and the coupling between Pt and P nuclei observed in the ^{31}P{^{1}H} NMR spectra of **3** has substantiated that the PPh$_3$ ligand binds to the Pt atom. The methyl protons in the S$_2$CNEt$_2$ ligands appeared as one signal, suggesting the equivalence of all methyl groups. This structural feature has been unequivocally confirmed by the X-ray analysis of **3b** described below.

X-ray Structure of 3b. Since high-quality single crystals were obtained for **3b**, an X-ray analysis was carried out to elucidate its structure in detail. An ORTEP drawing of **3b** is shown in Figure 1, while selected bond distances and angles are collected in Table 1. Cluster **3b** has a triangular PtW$_2$ core, in which the two Pt−W edges are each bridged by one μ_2-S ligand, whereas the remaining W−W edge is supported by two μ_2-S ligands. The two μ_2-S atoms bridging the Pt−W bonds and the three metal atoms are almost coplanar. Ignoring the orientation of the Ph groups in the PPh$_3$ ligand, **3b** may be considered to have a pseudo mirror plane defined by these five atoms along with the P atom, which is consistent with the spectral data shown above. The four-membered ring that comprises two W atoms and the two S atoms bridging the W−W edge is not flat but puckered with the dihedral angle of 149° along the W−W bond.

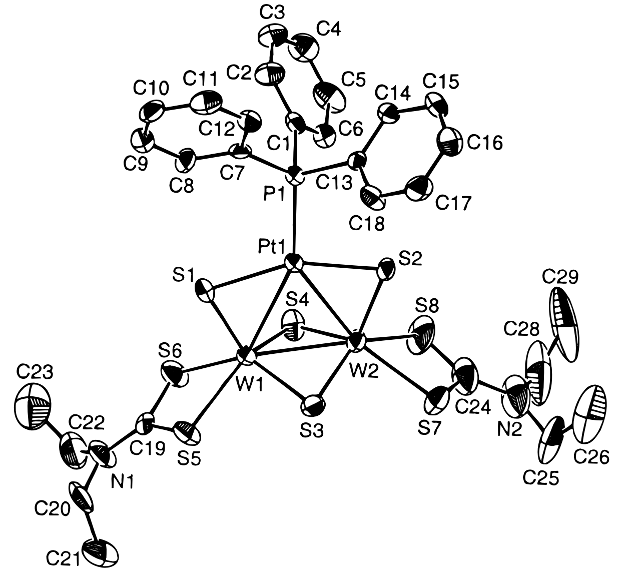


Figure 1. ORTEP drawing for **3b**. Disordered carbon atoms with lower occupancy in a diethyldithiocarbamato ligand (C(27) and C(30)) as well as hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles in **3b**

Bond Distances (Å)			
Pt(1)−W(1)	2.787(1)	Pt(1)−W(2)	2.796(1)
W(1)−W(2)	2.698(1)		
Pt(1)−S(1)	2.271(4)	Pt(1)−S(2)	2.269(4)
Pt(1)−P(1)	2.266(4)		
W(1)−S(1)	2.191(5)	W(2)−S(2)	2.182(4)
W(1)−S(3)	2.321(4)	W(2)−S(3)	2.311(5)
W(1)−S(4)	2.320(5)	W(2)−S(4)	2.316(5)
W(1)−S(5)	2.483(4)	W(2)−S(7)	2.457(6)
W(1)−S(6)	2.472(4)	W(2)−S(8)	2.458(6)
Bond Angles (deg)			
Pt(1)−W(1)−W(2)	61.28(3)	Pt(1)−W(2)−W(1)	60.93(3)
W(1)−Pt(1)−W(2)	57.79(3)		
S(1)−Pt(1)−P(1)	106.9(2)	S(2)−Pt(1)−P(1)	95.9(2)
S(1)−Pt(1)−S(2)	157.2(2)		
W(2)−W(1)−S(1)	113.9(1)	W(1)−W(2)−S(2)	113.3(1)
S(1)−W(1)−S(3)	117.3(2)	S(2)−W(2)−S(3)	113.8(2)
S(1)−W(1)−S(4)	114.3(2)	S(2)−W(2)−S(4)	117.0(2)
Pt(1)−W(1)−S(3)	86.2(1)	Pt(1)−W(2)−S(3)	86.2(1)
W(2)−W(1)−S(3)	54.2(1)	W(1)−W(2)−S(3)	54.5(1)
Pt(1)−W(1)−S(4)	83.3(1)	Pt(1)−W(2)−S(4)	83.2(1)
W(2)−W(1)−S(4)	54.4(1)	W(1)−W(2)−S(4)	54.5(1)

The W−W distance at 2.698(1) Å is slightly shorter than that in the parent **1b** (2.795(2) Å)[7] and the other ditungsten complexes containing the WS(μ_2-S)$_2$WS core such as [W$_2$S$_2$(μ_2-S)$_2$Cl$_2$(py)$_4$] (2.844(4) Å; py = pyridine),[8] [W$_2$S$_2$(μ_2-S)$_2$(S$_4$)$_2$]$^{2-}$ (2.836(2) Å),[9] and [W$_2$S$_2$(μ_2-S)$_2$(SCH$_2$CH$_2$S)$_2$]$^{2-}$ (2.862(1) Å),[10] but still significantly longer than the W−W double bond in, e.g., [W$_2$(μ_2-S)$_2$(μ_2-S$_2$CNEt$_2$)$_2$(S$_2$CNEt$_2$)$_2$] (2.530(2) Å).[11] The two Pt−W distances at 2.787(1) and 2.796(1) Å are comparable to the typical Pt−W bond distances (2.663−2.895 Å).[12]

The significantly long separation of the Pt atom from both of the two μ_2-S atoms bridging the W−W bond (3.41 and 3.51

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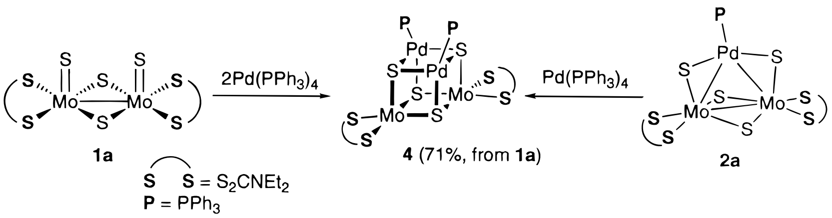
Scheme 1



Å) clearly distinguishes the PtW_2S_4 core in **3b** from the typical $M_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3$ incomplete cubane-type cores. Thus, neglecting the metal−metal bonds, the coordination geometry around the Pt atom is distorted square planar with the void site opposite to the P atom (S(1)−Pt−P, 106.9(2)°; S(2)−Pt−P, 95.9(2)°), whereas that around the two W atoms is distorted square pyramidal. The distances of the W(1)−S(1) and W(2)−S(2) bonds (2.191(5) and 2.182(4) Å) are elongated from the corresponding W═S bond distances in **1b** (2.086 Å (mean)).[7] However, they are still considerably shorter than those of the other four $W-\mu_2\text{-}S$ lengths (2.311(5)−2.321(4) Å) and rather close to those of the typical terminal W═S bonds (2.01−2.19 Å).[13] This might indicate the donation of the lone-pair electron on the S(1) or S(2) atom to the W atom. The $Pt-\mu_2\text{-}S$ distances of 2.271(4) and 2.269(4) Å are slightly shorter than those in some Pt(II) complexes without any metal−metal interactions around the Pt atom(s) such as $[(Ph_3P)_2Pt(\mu_2\text{-}S)_2(Cp^*Ru)_2(\mu_2\text{-}SPr^i)_2]$[14a] and $[Pt_2(\mu_2\text{-}S)_2(dppy)_4]$[14b] (2.31−2.36 Å; dppy = 2-diphenylphosphinopyridine).

Dinuclear sulfido complexes with a M_2S_4 core are now known to serve as useful precursors to prepare mixed-metal sulfido clusters with a variety of core structures.[15−20] However, to our knowledge, incorporation of one heterometal into the $M_2S_2(\mu_2\text{-}S)_2$ cores have so far resulted in the formation of the $M_2M'(\mu_3\text{-}S)(\mu_2\text{-}S)_3$ incomplete cubane-type clusters exclusively, and the $Pt(\mu_2\text{-}S)_2W_2(\mu_2\text{-}S)_2$ core found in **3b** is unprecedented for M_3S_4 clusters. For example, the reactions of $[Et_4N]_2[M_2S_2(\mu_2\text{-}S)_2(SCH_2CH_2S)_2]$ (M = Mo, W) with $[Cu\{S_2P(OEt)_2\}(PPh_3)_2]$ or $[Ag(NO_3)(PPh_3)_3]$ are known to afford the mixed-metal sulfido clusters $[Et_4N][(Ph_3P)M'M_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3(SCH_2CH_2S)_2]$ (M′ = Cu, Ag).[16a−c]

Preparation of $Pd_2Mo_2S_4$ Cubane-Type Cluster 4. When **1a** was treated with 2 equiv of $[Pd(PPh_3)_4]$, the mixed-metal sulfido cluster with a cubane-type $Pd_2Mo_2S_4$ core $[\{Pd(PPh_3)\}_2\{Mo(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (**4**) was obtained in 71% yield (Scheme 1). The IR spectrum of **4** indicates disappearance of the Mo═S bonds in **1a**. In contrast to **2a**, however, the ^1H and $^{31}P\{^1H\}$ NMR spectrum shows the presence of the S_2CNEt_2 and PPh_3 ligands in a ratio of 1:1. Cluster **4** seems to be produced via initial formation of the triangular cluster **2a**. Indeed, further addition of $[Pd(PPh_3)_4]$ to a mixture of **2a** and **4** prepared as described above afforded a product solution containing **4** as the only metal species from the ^1H and $^{31}P\{^1H\}$ NMR criteria.

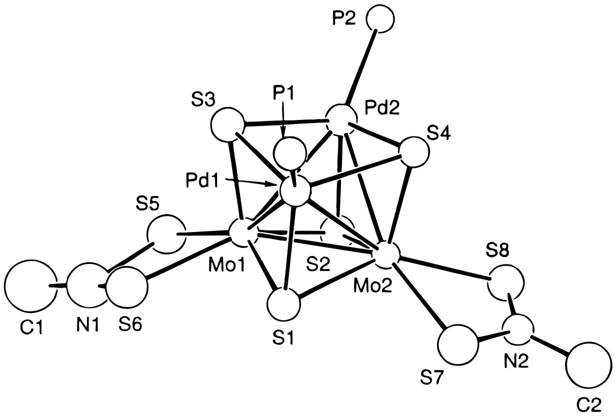


Figure 2. Molecular structure of **4**. Phenyl and ethyl groups are omitted.

Unfortunately, the related cubane-type clusters were not isolated from other combinations of **1** and 2 equiv of $[M'(PPh_3)_4]$ (M′ = Pd, Pt). Thus, from the reaction of **1b** and $[Pt(PPh_3)_4]$, only the triangular **3b** was isolated, while analogous treatment of **1a** with $[Pt(PPh_3)_4]$ and **1b** with $[Pd(PPh_3)_4]$ both resulted in the formation of complex mixtures of unidentified products. For the latter reaction, formation of the cubane-type cluster $[\{Pd(PPh_3)\}_2\{W(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (**5**) is suggested by the ^1H and $^{31}P\{^1H\}$ NMR spectra of the reaction mixture. Furthermore, its structure has been confirmed by the X-ray analysis using a single crystal of the product accidentally isolated in quite a low yield. However, cluster **5** obtained in a crude form was readily converted to an uncharacterizable species during the recrystallization, and we have not yet succeeded in finding the procedure to isolate **5** in a pure form and in a reproducible way.

The cubane-type structure of **4** has been confirmed further by a preliminary X-ray diffraction study using a single crystal of **4**, although refinement of the structure was unable to be completed due to the poor reflection data.[21] However, the atom-connecting scheme for the pertinent part of **4** has been clarified by the preliminary result, as shown in Figure 2. Cluster **4** has an approximate C_{2v} symmetry with a 2-fold axis passing through the midpoints both between two Pd atoms and between two

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(21) Unit cell parameters for **4**: orthorhombic, space group $P2_12_12_1$ with a = 16.97(1) Å, b = 29.31(1) Å, c = 11.07(2) Å, V = 5507(8) Å^3. Substitution of the PPh_3 ligand in **4** by CO, alkynes, alkenes, and $PMePh_2$ has been attempted in order to obtain high-quality single crystals suitable for X-ray analysis, but it has been unsuccessful.

Mo atoms. With respect to the Pd_2Mo_2 core, it appears that there is bonding interaction between the two Mo atoms and between the Mo and Pd atoms, but not between two Pd atoms. The tetrametallic framework is therefore viewed as a butterfly structure with two Pd atoms at the wing-tip positions. Each Pd atom is bound to three μ_3-S atoms and one PPh_3 ligand in a tetrahedral manner, whereas each Mo atom displays square pyramidal configuration surrounded by five sulfur atoms.

Preparation of $M_2M'_2S_4$ cubane-type clusters from dinuclear precursors containing $M_2S_2(\mu_2\text{-}S)_2$ cores has already been demonstrated. For example, **1** is known to react with $[Co_2(CO)_8]$ to give $[\{Co(CO)\}_2\{M(S_2CNEt_2)(\mu_3\text{-}S)_4(MeCN)\}_2]$ (M = Mo, W), in which six metal−metal bonds exist.[15] Furthermore, formation of $[\{Cu(PPh_3)\}_2\{M(SCH_2CH_2S)\}_2(\mu_3\text{-}S)_4]$ (M = Mo, W) from $[Et_4N]_2[M_2S_2(\mu_2\text{-}S)_2(SCH_2CH_2S)_2]$ and 2 equiv of $[CuCl(PPh_3)_3]$ has also been reported,[16d] which has a butterfly metal core similar to that in **4**. However, incorporation of noble metals into $M_2S_2(\mu_2\text{-}S)_2$ cores to give $M_2M'_2S_4$ cubane-type clusters is unprecedented.

Facile formation of **4** from **2a** and $[Pd(PPh_3)_4]$ may suggest that **2** and **3** serve as the potential precursors for preparing cubane-type $M^1M^2M_2S_4$ clusters containing three different metals (M = Mo, W; M^1, M^2 = Pd, Pt). As to a related reaction, synthesis of $[CuWMo_2(\mu_3\text{-}S)_4(\mu_2\text{-}S_2PR_2)(S_2PR_2)_3I]$ (R = Et, Pr^n) by stepwise incorporation of heterometals into $[Mo_2S_2(\mu_2\text{-}S)_2(S_2PR_2)_2]$ has been reported.[22] In contrast to the ready conversion of **2a** into **4** by treatment with additional $[Pd(PPh_3)_4]$, however, reaction of **2** with $[Pt(PPh_3)_4]$ resulted in the formation of only the intractable products, whereas the reaction of **3a** with $[Pd(PPh_3)_4]$ afforded the Pd_2Mo_2 cluster **4**, for which the fate of the Pt atom is uncertain.

At present, the oxidation states of the metals in these novel clusters described here are unclear. The XPS analyses for **2a** and **4** have been carried out to obtain some information about the oxidation states; the Pd-$3d_{5/2}$ binding energies for both **2a** (336.4 eV) and **4** (336.5 eV) lie between the values for Pd(0) (e.g. $[Pd(PPh_3)_4]$: 335.9 eV) and Pd(II) (e.g. $[PdCl_2(PPh_3)_2]$: 338.0 eV). On the other hand, preliminary extended Hückel molecular orbital calculations for $[Pt(PH_3)(\mu_2\text{-}S)_2\{W(S_2CNMe_2)\}_2(\mu_2\text{-}S)_2]$ and $[\{Pd(PH_3)\}_2\{Mo(S_2CNMe_2)\}_2(\mu_3\text{-}S)_4]$, based on the structures of **3b** and **4**, suggest that both **3b** and **4** contain the d^{10} Pt(Pd) and d^1 W(Mo) centers. These results indicate that some ambiguity about the oxidation state of the metals still remains, and thus we are continuing further investigations to determine the oxidation states.

In summary, we have prepared a series of noble-metal sulfide clusters **2** and **3** with unprecedented $M'(\mu_2\text{-}S)_2M_2(\mu_2\text{-}S)_2$ triangular cores along with the cubane-type cluster **4** through incorporation of noble metals into the dinuclear cores in **1**. Remarkable dependence of the produced cluster cores on the kind of noble metals is noteworthy. Further studies are in progress, which are directed toward the preparation of sulfido clusters containing noble metals other than palladium and platinum as well as reactivities of the noble-metal sulfide clusters obtained through these synthetic pathways.

Experimental Section

General Methods. All reactions were carried out under dry nitrogen atmosphere by using standard Schlenk techniques. Solvents were dried by the usual methods and distilled before use. Complexes $[M_2S_2(\mu_2\text{-}S)_2(S_2CNEt_2)_2]$ (M = Mo,[23] W[9]), $[Pd(PPh_3)_4]$,[24] and $[Pt(PPh_3)_4]$[25] were prepared according to the literature. IR spectra were obtained from a Shimadzu FTIR-8000M spectrometer, while ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL EX-270 or LA-400 spectrometer. UV−visible spectra were measured by a Shimadzu UV-2400PC spectrometer, and elemental analyses were performed by a Perkin-Elmer 2400 series II CHN analyzer. XPS analyses were measured by a Kratos XSAM800pci spectrometer.

Preparation of $[M'(PPh_3)(\mu_2\text{-}S)_2\{M(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ (2, M′ = Pd, M = Mo, W; 3, M′ = Pt, M′ = Mo, W). The following procedure for the preparation of $[Pd(PPh_3)(\mu_2\text{-}S)_2\{W(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ (**2b**) is representative. A mixture of **1b** (800 mg, 1.01 mmol) and $[Pd(PPh_3)_4]$ (1.17 g, 1.01 mmol) in THF (200 mL) was stirred at room temperature for 17 h, and the solvent was removed in vacuo. The residual purple powder was extracted with 150 mL of benzene. Addition of hexane to the concentrated extract gave **2b** as purple crystals (787 mg, 67%). ^1H NMR ($CDCl_3$): δ 1.40 (dd, 12 H, NCH_2CH_3), 3.86−4.03 (m, 8 H, NCH_2CH_3), 7.20−7.58 (m, 15 H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 69.0 (s, PPh_3). UV−visible (λ_{max}, nm (ϵ, M^{-1} cm^{-1}), CH_2Cl_2): 398 (7600), 560 (3900). Anal. Calcd for $C_{28}H_{35}N_2PS_8W_2Pd$: C, 28.96; H, 3.04; N, 2.41. Found: C, 28.86; H, 2.99; N, 2.30.

Preparation of $[Pt(PPh_3)(\mu_2\text{-}S)_2\{Mo(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ (3a). Green crystals (64%). ^1H NMR ($CDCl_3$): δ 1.42 (dd, 12 H, NCH_2CH_3), 3.97−4.18 (m, 8 H, NCH_2CH_3), 7.18−7.29 (m, 15 H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.5 (s, PPh_3, J_{PtP} = 4381 Hz). UV−visible (λ_{max}, nm (ϵ, M^{-1} cm^{-1}), CH_2Cl_2): 412 (5700), 669 (4100). Anal. Calcd for $C_{28}H_{35}N_2PS_8Mo_2Pt$: C, 31.31; H, 3.28; N, 2.61. Found: C, 31.38; H, 3.26; N, 2.48.

Preparation of $[Pt(PPh_3)(\mu_2\text{-}S)_2\{W(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ (3b). Purple crystals (84%). ^1H NMR ($CDCl_3$): δ 1.43 (dd, 12 H, NCH_2CH_3), 3.89−4.09 (m, 8 H, NCH_2CH_3), 7.21−7.36 (m, 15 H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 74.8 (s, PPh_3, J_{PtP} = 4223 Hz). UV−visible (λ_{max}, nm (ϵ, M^{-1} cm^{-1}), CH_2Cl_2): 385 (11 000), 573 (6400). Anal. Calcd for $C_{28}H_{35}N_2PS_8W_2Pt$: C, 26.91; H, 2.82; N, 2.24. Found: C, 26.85; H, 2.77; N, 2.15.

Reaction of 1a with 0.8 Equiv of $[Pd(PPh_3)_4]$. A mixture of **1a** (61.7 mg, 0.100 mmol) and $[Pd(PPh_3)_4]$ (92.4 mg, 0.80 mmol) in THF (20 mL) was stirred at room temperature for 6 h, and the solvent was removed in vacuo. The ^1H and $^{31}P\{^1H\}$ NMR spectra showed that the resultant solid contains $[Pd(PPh_3)(\mu_2\text{-}S)_2\{Mo(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ (**2a**) and $[\{Pd(PPh_3)\}_2\{Mo(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (**4**; vide infra) in the ratio of ca. 10:1. Data for **2a**, ^1H NMR ($CDCl_3$): δ 1.40 (dd, 12 H, NCH_2CH_3), 3.93−4.10 (m, 8 H, NCH_2CH_3), 7.24−7.31 (m, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 46.6 (s, PPh_3). UV−visible (λ_{max}, nm, CH_2Cl_2): 441, 654.

Preparation of $[\{Pd(PPh_3)\}_2\{Mo(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$ (4). A mixture of **1a** (886 mg, 1.44 mmol) and $[Pd(PPh_3)_4]$ (3.33 g, 2.88 mmol) in THF (200 mL) was stirred at room temperature for 22 h, and the solvent was removed in vacuo. Recrystallization from CH_2Cl_2−hexane afforded black crystals (1.38 g, 71%). ^1H NMR ($CDCl_3$): δ 1.30 (dd, 12 H; NCH_2CH_3), 3.81−3.86 (m, 8 H, NCH_2CH_3), 7.27−7.64 (m, 30 H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.2 (s, PPh_3). UV−visible (λ_{max}, nm, CH_2Cl_2): 456 (sh), 507 (sh). Anal. Calcd for $C_{46}H_{50}N_2P_2S_8Mo_2Pd_2$: C, 40.80; H, 3.72; N, 2.07. Found: C, 40.20; H, 3.83; N, 2.21.

X-ray Diffraction Studies. Cluster **3b** prepared as described above was recrystallized from CH_2Cl_2−ether to give single crystals suitable for the X-ray analysis, one of which was sealed in a glass capillary under N_2 and transferred to a Rigaku AFC7R diffractmeter equipped with a graphite-monochromatized Mo Kα source. Diffraction study was carried out at room temperature. Orientation matrixes and unit cell parameters were determined by least-squares treatment of 21 reflections with $29.2 < 2\theta < 29.9°$. The intensities of three check reflections were monitored every 150 reflections during data collection, which revealed no significant decay. Intensity data were corrected for Lorentz−polarization effects and for absorption (ψ scans). Details of crystal and data collection parameters are summarized in Table 2. Structure solution and refinements were carried out by using the teXsan

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Table 2. X-ray Crystallographic Data for **3b**

empirical formula	$C_{28}H_{35}N_2PS_8W_2Pt$
fw	1249.84
space group	$C2/c$ (No. 15)
a/Å	13.718(3)
b/Å	12.795(2)
c/Å	43.798(2)
β/deg	95.24(1)
V/Å^3	7654(1)
Z	8
λ/Å	0.710 69
ρ_{calcd}/g cm^{-3}	2.169
μ(Mo Kα)/cm^{-1}	101.35
transm factors	0.2407−0.9990
R_{int}	0.086
R^a	0.052
$R_w{}^b$	0.038

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

program package.[26] The positions of heavy atoms were determined by Patterson methods and subsequent Fourier syntheses (DIRDIF PATTY).[27] In the final Fourier map, two of the terminal carbon atoms in a diethyldithiocarbamato ligand were found at two disordered positions each and were refined as C(26), C(29), C(27), and C(30) with the occupancy of 60% for the former two atoms and 40% for the latter two ones. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques (based on F). All hydrogen atoms except for those attached to C(25) and C(28) were placed at the calculated positions and included in the final stage of refinement with fixed parameters. The atomic scattering factors were taken from ref 28, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 29.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available for **3b** on the Internet only. Access information is given on any current masthead page.

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